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THE NITROSULPHONIC ACIDS OF PARAXYLENE

DISSERTATION

Submitted to the Faculty of the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

By

RALPH CHASE HUSTON

June 1914

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INTRODUCTION.

The nitrosulphonic acids of metaxylene have been quite thoroughly studied. Simonsen (Trans., 103, 1144) has prepared three nitrosulphonic acids of orthoxylene while those derived from paraxylene have been studied to a very slight extent.

Nolting and Kohn (Ber., 19, 141) record the preparation of an aminosulphonic acid of paraxylene to which they assign the formula,

$$C_6H_2(CH_3)_2NH_2SO_3H$$
(1.4 6 2)

This acid was prepared by reducing with ammonium sulphide or with tin and hydrochloric the solution resulting from the treatment of p-xylene-sulphonic acid with red fuming nitric acid. The nitro acid was not isolated or studied nor were any of its derivatives prepared. No other record was found in the literature of the preparation or study of this or any other nitrosulphonic acid of p-xylene.

Guy G. Frary in his unpublished Master's Thesis (S. U. I., 1909) describes a nitrosulphonic acid of p-xylene which he prepared by nitrating p-xylenesulphonic acid with nitric acid (sp. gr. 1.60) in the cold. The acid separated out on standing at room temperature in radiating tufts of needles which were extremely soluble in water and alcohol but

insoluble in ether, petroleum ether, chloroform, and carbon tetrachloride. The solubility in water was lessened by the presence of nitric or hydrochloric acids but increased by the presence of sulphuric acid. The potassium, sodium, calcium, barium, strontium, magnesium, copper, and zinc salts were prepared and of these the potassium, barium, copper, and zinc salts were analyzed. Most of these were prepared from the crude acid solution and were purified with difficulty. Frary assigned the formula

$$C_6H_2(CH_3)_2NO_2SO_3H$$
(1-4 6 2)

to the acid in spite of the fact that an attempt to reduce it to the amino acid, prepared by Nolting and Kohn, proved unsuccessful. Attempts to prepare the sulphonchloride by treating the free acid or the potassium salt with phosphorus pentachloride resulted in each case in the formation of a reddish brown oil which failed to solidify under water and which did not crystallize from dry ether, carbon tetrachloride, chloroform or a mixture of ether and petroleum ether. Somewhat better success attended the attempts to prepare the sulphonchloride of the nitrosulphonic acid by nitrating the sulphonchloride p-xylene with nitrosulphuric acid. Two nitrosulphonchlorides were obtained by this method. One was obtained in quantities large enough for analysis; it melted at 109.5° and gave an amide melting at 179°. The other, and more soluble nitrosulphonchloride, was obtained in an insufficient quantity for analysis. It melted at 56°-57° and gave an amide which melted at 199°-200°. A sulphonanilide, which had after three crystallizations a melting point of 136°-137°, was also prepared from the oily sulphonchloride.

It is evident from the foregoing paragraphs that our knowledge of the nitrosulphonic acids of p-xylene is very limited. With the hope of obtaining a more thorough knowledge of these compounds the following research was undertaken:

The problem was attacked in two ways, the initial material in each case being "Kahlbaum's" paraxylene. In one series of experiments p-xylene was sulphonated and various methods of nitration were tried on the sulphonic acid thus formed, or on its chloride. In the other series a nitro group was introduced into p-xylene and the nitro-p-xylene then treated with different concentrations of sulphuric acid or with chlorsulphonic acid.

SULPHONATION OF PARAXYLENE.

P-xylene is less readily attacked by ordinary concentrated sulphuric acid than either of the other xylenes. M-xylene is completely dissolved by shaking it with the acid for a few hours at room temperature, while O-xylene is readily sulphonated at slightly elevated temperatures.

The commercial method of preparing p-xylene by treating the crude xylene obtained from coal tar with warm sulphuric acid has been shown by Nolting and Witt (Ber. 18, 2664) to be imperfect. They found that when xylidine, prepared from commercial xylene, is sulphonated at least twenty-five per cent of the product is a derivative of p-xylene. This is a much larger per cent than is obtained by the separation of the xylenes by sulphonation. It therefore follows that p-xylene is attacked to a considerable extent at the temperature of boiling water by concentrated sulphuric acid.

Fittig and Glinzer (Ann. 136, 305) and Jacobson (Ber. 10, 109) sulphonated p-xylene by means of strongly fuming sulphuric acid. Frary (Thesis, 1909) obtained satisfactory results by using mixtures of concentrated and seventy per cent fuming sulphuric acids. For example, he heated 100 g. p-xylene and 175 g. sulphuric acid (sp. gr. 1.84) on a water bath, with occasional shaking, for thirty-six hours. At the end of this time about half of the xylene was dissolved. He then added a mixture of 40 g. of concentrated and 20 g. of seventy per cent fuming sulphuric acids and obtained complete sulphonation in a few hours. In another trial Frary added in small portions and with continual shaking a mixture of 200 g. of sulphuric acid (sp. gr. 1.84) and 25 g. of fuming sulphuric acid (70%), to 100 g. of p-xylene. The xylene went into solution readily with considerable evolution of heat.

In the present investigation fuming sulphuric acid containing twenty-five per cent of anhydride was used as a sulphonating agent. This acid was prepared by dissolving the calculated amount of solid sulphur trioxide in concentrated sulphuric acid. Since, as is evident from the work of Frary, a thorough mixing of the materials is an important factor in the sulphonation, a rotator, driven by a motor so that the materials could be constantly agitated, was used. The sulphonation was carried out as follows: 500 g. of p-xylene, in a glass stoppered bottle, was treated with 650 g. of fuming sulphuric acid (25% anhyd.). The acid was added in small portions at a time and the mixture shaken constantly. Considerable heat was evolved, but the acid was added slowly and in such quantities that the temperature did not rise over 65° C. On standing over night about three-fourths of the p-xylene dissolved. 75 g. more

of the acid was added and the mixture turned in the rotator three hours, at the end of which time sulphonation was complete. The light brown syrupy mass (1075 c. c.) was poured into an equal volume of water, stirred and allowed to stand over night. The separated acid was filtered off by suction and dried on porous plates. Yield 770 g. The mother liquor yielded, on being heated two hours and cooled, a second crop of crystals which weighed 220 g., making a total of 990 g. of the crude sulphonic acid. A thrid crop of crystals, which tended to come down in radiating tufts, was obtained from the mother liquor. This compound was not studied further.

A small portion of the p-xylenesulphonic acid was purified by dissolving it in water and precipitating with hydrochloric acid gas. After four re-precipitations it melted at 87°-88°. The acid used for nitration was not purified further than the first precipitation, and contained a considerable amount of sulphuric acid. In one or two cases the nitrating agent was added to the crude solution of sulphonic acid, no previous precipitation being made.

NITRATION OF PARAXYLENESULPHONIC ACID.

The method recorded by Frary, through which he succeeded in nitrating the sulphonic acid of p-xylene, resembles very closely the method used by Claus and Schmidt (Ber. 19, 1418) in nitrating the sulphonic acid of m-xylene. It differs from the method of Nolting and Kohn (Ber. 19, 143) in that heat is not applied to the reacting mixture until the reaction is almost complete. The crude p-xylenesulphonic acid was treated with two and one-half times

its weight of red fuming nitric acid with or without cooling. The reaction began gently but increased in violence, raising the temperature to about 50°. The resulting red liquid was heated on the water bath and freed from nitric fumes by diluting with water and subsequently evaporating to small bulk. The acid separated from the very concentrated solution after standing for some time at room temperature. An attempt to nitrate the sulphonic acid of p-xylene, by means of a mixture of nitric acid (sp. gr. 1.52) and acetic anhydride was not successful in the hands of Frary.

In the work here described three methods were used for nitrating the sulphonic acid. In all of them fuming nitric acid was the nitrating agent.

First Method: 100 g. of the crude p-xylenesulphonic acid was treated with 185 g. of fuming nitric acid (sp. gr. 1.51), a little at a time being added. The crystals of sulphonic acid were dissolved, red fumes were evolved, and the temperature reached 55°. When all of the nitric acid had been added, the solution was evaporated on a water bath to a thick syrup, diluted with water to 500 c. c. and again evaporated to 150 c. c. Upon the addition of an equal volume of saturated potassium chloride solution the potassium salts of the sulphonic acids began to separate at once in small nodules, hydrochloric acid being evolved. After two days they were filtered off by suction and dried on porous plates. Yield, 48 g.

Second Method: 100 c. c. of the syrupy solution produced by the sulphonation of p-xylene was treated with nitric acid (sp. gr. 1.51), drop by drop, until 45 c. c. had been added. The containing flask was cooled in ice during the addition of the nitric acid. The reaction proceeded

slowly with evolution of red fumes. When all of the acid had been added the solution was allowed to stand over night. (It became pasty due to the partial separation of crystals.) After being evaporated on the water bath until red fumes ceased to be evolved, it was poured into 600 c. c. of water. A small amount of dinitro-p-xylene, which separated out, was filetred off and the solution again evaporated to 110 c. c. 110 c. c. of potassium chloride solution was added and the mixture allowed to stand two days. The potassium salt was then filtered off and air-dried. Yield, 64 g.

Third Method: 100 g. of the dry crude p-xylenesulphonic acid was treated in the cold with a mixture of 125 g. of nitric acid (sp. gr. 1.51) and 75 g. of sulphuric acid (sq. gr. 1.84). The reaction was quite violent at first but moderated so that the last half of the nitrosulphuric acid could be added without cooling. After being heated on the water bath three hours to drive off the oxides of nitrogen the solution was diluted to 900 c. c. and evaporated to 160 c. c. The potassium salts were then precipitated as in the other methods. Yield, 43 g.

Of the three methods, the second is preferable as it gives the largest yield and the potassium sulphonates come down comparatively free from potassium sulphate.

ACTION OF PHOSPHOROUS PENTACHLORIDE ON THE POTASSIUM SALTS OF THE NITROSULPHONIC ACIDS.

Frary's failure to obtain crystalline sulphonchlorides by the action of phosphorous pentachloride on the crude potassium salts of the nitrosulphonic acids is hard to understand. In this investigation eleven experiments, in which

the dry potassum salts were treated with phosphorous pentachloride under different conditions, were made. All of the experiments yielded two sulphonchlorides, one melting at 109.5° and a more soluble one melting at 60°, while four of the eleven yielded in addition a third sulphonchloride, in very small amounts, which melted at 75°. The best yields were obtained under the following conditions: 150 g. of the crude powdered potassium salts of the nitrated sulphonic acid, dried at 110°, was treated with 200 g. of phosphorous pentachloride. Heat was evolved and the entire mass slowly liquified. After standing two hours the containing flask was heated one hour on the water bath. The heavy oily liquid was poured into ice water, washed thoroughly, and allowed to stand under ice water two days. It did not solidify but became granular in appearance and of the consistency of thick paste. After the water was drained off the paste was dissolved in 1000 c. c. of ether and dried over calcium chloride. Most of the ether was distilled off and the residue transferred to a beaker. Crystals began to form almost immediately although very slowly. After standing ten days the crystals were filtered off by the aid of a suction pump and washed with a mixture of ether and petroleum ether. Yield, 10.5 g. From this batch of crystals, upon recrystallization from ether and petroleum ether, there were obtained two sulphonchlorides: 9.6 g. of one which gave a melting-point of 109.5°, and 0.2 g. of a slightly more soluble one which melted at 74.5°. (In one case the separation of the two sulphonchlorides was made mechanically.) The mother liquor from the first crop of crystals was placed in an ice box for three weeks, when a second crop of crystals was filtered off. This crop gave, on recrystallization, 2.3 g. of the sul-

phonchloride melting at 109.5° and 3.1 g. of a decidedly more soluble sulphonchloride of the same crystal form which, after repeated recrystallization, melted at 60°. The mother liquor was again placed on ice and allowed to stand one month. A third crop of crystals of the sulphonchloride melting at 60° was obtained. Yield, 10.4 g. The remaining 14 g. of reddish oil did not yield crystals on standing three months. When treated with ammonium hydroxide it gave an amide which melted, after seven recrystallizations from alcohol and water, at 147°, a close agreement with the melting point of p-xylenesulphonamide.

Total yield of the nitrosulphonchloride melting at ~~60°~~ 109.5° = ~~13.5~~ 11.9 g.

Total yield of the nitrosulphonchloride melting at 75° = 0.2 g.

Total yield of the nitrosulphonchloride melting at 60° = 13.5 g.

An attempt to increase the rate of precipitation of the low melting nitrosulphonchloride by dissolving the oil in ether, shaking with dilute ammonium hydroxide, neutralizing with hydrochloric acid, drying and evaporating, was not successful.

Recrystallization of the crude potassium salts from alcohol did not increase the yield of nitrosulphonchlorides to an appreciable extent.

NITRATION OF THE SULPHONCHLORIDE OF PARAXYLENE.

Although Frary tried several times to nitrate p-xylenesulphonchloride, he succeeded in doing so only once. In this successful experiment he treated 10 g. of the sulphonchloride with a mixture of 8 g. of red fuming nitric acid

and 6 g. of concentrated sulphuric acid. He heated the mixture on the water bath, poured it into cold water and dissolved the solidified oil in ether. He then recrystallized it from a mixture of ether and petroleum ether. The yields of the two nitrosulphonchlorides were not recorded but they were small.

Below are given the results of five experiments in which the sulphonchloride of p-xylene was treated with nitrating agents of different kinds and concentrations. The p-xylenesulphonchloride was prepared by treating the dried p-xylenesulphonic acid with an excess (2 mols.) of phosphorous pentachloride and heating on the water bath. It was purified by washing with ice water, dissolving the residue in ether, drying the solution over fused calcium chloride, filtering and distilling off the ether.

First Experiment: 10 g. of p-xylenesulphonchloride, in a beaker, was treated with 5 g. of nitric acid (sp. gr. 1.51). A brisk reaction set in with evolution of red fumes. The mixture divided itself into two layers. After standing at room temperature the beaker was heated for two hours on the water bath with occasional shaking. When poured into ice water the upper layer sank as an oil to the bottom and solidified in about fifteen minutes while the lower layer left a light milky precipitate. The solid was filtered off, dissolved in ether and dried over calcium chloride. The calcium chloride was filtered off and the solution evaporated at room temperature. After six days a few characteristic crystals of the sulphonchloride which melts at 109.5° formed on the sides of the beaker. The oil yielded no more crystals on standing three weeks at low temperature. Yield, 0.15 g.

Second Experiment: 10 g. of p-xylenesulphonchloride was treated with a mixture of 5 g. of nitric acid (sq. gr. 1.51) and 3 g. of concentrated sulphuric acid. A rather more violent reaction than resulted from the use of nitric acid alone set in and two layers were formed. After heating two hours on the water bath the mixture was poured into ice water. As in the first experiment the upper layer formed an oil which solidified on standing while the lower layer formed a milky precipitate. The wash water was extracted with ether and the solidified oil dissolved in the same ether. After drying over calcium chloride the solution was evaporated for five days in a current of dry air, when crystals of the nitrosulphonchloride melting at 109.5° began to separate. On standing four days longer they were filtered off and the oily mother liquor was placed in the ice box. No more crystals formed on standing three weeks. Yield, 0.42 g.

Third Experiment: 10 g. of p-xylenesulphonchloride was treated with a mixture of 10 g. of nitric acid (sq. gr. 1.51) and 6 g. of concentrated sulphuric acid. A decidedly vigorous reaction set in, the upper layer of the reacting mixture disappearing into the lower layer. After the violence of the reaction had subsided the beaker was heated one hour on the water bath. When poured into water no oil separated but a finely divided precipitate gave the water a milky appearance. On extracting with ether, drying, and evaporating the solvent, a somewhat larger yield of the high melting nitrosulphonchloride was obtained, i. e., 1.05 g. in five days. As no more crystals separated from the oily mother liquor on standing in the ice box two weeks, it was washed thoroughly with water, dissolved again in ether and dried over calcium chloride. This time crystals

began to separate slowly after three days. The total yield after two weeks was 0.2 g. The crystals melted after two recrystallizations from ether at 59°.

Washing the residual oils of the two preceding experiments did not cause the separation of any of the low melting nitrosulphonchloride.

The above experiment was repeated several times with results comparable to those recorded in all cases except the one which is described briefly here: 10 g. of p-xylenesulphonchloride was treated with nitric and sulphuric acids as in the above experiment. An exceedingly vigorous reaction set in and the beaker was cooled in ice. As the reaction proceeded, the *lower* layer disappeared into the *upper*. After warming on the water bath the liquid was poured into ice water. No oil separated and the water turned only slightly turbid. On extracting with ether and proceeding as before, less than 0.1 g. of the high melting sulphonchloride was obtained.

Fourth Experiment: 10 g. of p-xylenesulphonchloride was treated with a mixture of 5 g. of nitric acid (sp. gr. 1.51) and 5 g. of acetic anhydride. The reaction proceeded smoothly, with evolution of red fumes, and the temperature rose to 60°. After standing one hour the beaker was heated two hours on the water bath and the contents poured into ice water. The oil solidified almost immediately, while the water remained only slightly turbid. The solidified oil yielded on dissolving in ether, drying and evaporating the solvent, 0.25 g. of the high melting sulphonchloride. Neither of the low melting sulphonchlorides was formed.

Fifth Experiment: 10 g. of p-xylenesulphonchloride was treated with a mixture of 9 g. of nitric acid (sp. gr. 1.51) and 10 g. of acetic anhydride, under the conditions

described in the preceding experiment. The reaction was somewhat more violent and only a small amount of oil separated out under water. This, on recrystallization from ether, yielded only a few crystals of the high melting sulphonchloride.

NITRATION OF PARAXYLENE.

In the nitration of p-xylene the temperature maintained during the reaction is an important factor in determining the product formed. Fittig and Glinzer (Ann. 136, 307), Lellman (Ann. 228, 250) and Nolting and Geissmann (Ber. 19, 144) have found that when p-xylene is warmed with excess of fuming nitric acid, with or without sulphuric acid, dinitro substitution products are formed in almost quantitative yields. On the other hand Jannasch (Ann 176, 55) was able to prepare the mononitro derivative by dropping into p-xylene, cooled in ice, an excess of fuming nitric acid.

The nitro-p-xylene used in the sulphonation experiments described under the two succeeding headings was prepared by a method similar to that of Jannasch. 100 g. of p-xylene, in a round bottomed flask, was cooled in ice and treated with small quantities of fuming nitric acid (sp. gr. 1.60) until 250 g. had been added. Some heat was generated and red fumes were given off, and, when the acid was added slowly, the reaction was perfectly smooth. The reacting mixture was allowed to stand over night, surrounded by ice, and was then poured into water. The oil which separated out was washed twice with water to rid it of excess nitric acid, then purified by distillation in a current of steam. The nitro-p-xylene, with some unchanged

p-xylene, passed over leaving a small amount of tarry matter in the flask. The crude product was finally heated to 220°, to drive off the unchanged p-xylene, and redistilled with steam. Yield of purified nitro-p-xylene (b. pt. 232°-238°), 93 g.

An attempt was made to prepare nitro-p-xylene by the action of Pictet's diacetyl orthonitric acid (Ber. 35, 2526) on p-xylene: 25 g. of p-xylene, dissolved in an equal weight of glacial acetic acid, was treated with a mixture of 60 g. of nitric acid (sp. gr. 1.51) and 75 g. of glacial acetic acid. No reaction occurred when the mixture was allowed to stand five hours at room temperature. When heated on the water bath reaction began at once with evolution of red fumes. After heating four hours to complete the reaction the mixture was poured into 500 c. c. of water. Fine light yellow crystals separated out. These were filtered by suction and washed repeatedly with cold water. Recrystallized from ether, the compound gave a melting point of 98°-99°. On dissolving in glacial acetic acid and evaporating, flat needles separated out which melted at 123°. The original precipitate was therefore a double compound of 2,6-dinitro-p-xylene and 2,3-dinitro-p-xylene. (Barner, Ber. 15, 2302, and Nolting and Geissman, Ber. 19, 144.) Yield, 32 g. 8.5 g. of mononitro-p-xylene settled out of the filtrate and washings from the dinitro compound. This was purified by distillation with steam.

ACTION OF SULPHURIC ACID ON NITROPARAXYLENE.

It is comparatively easy to nitrate the sulphonic acid of benzene or its homologues. It would seem, however, from the literature that it is difficult to sulphonate an

aromatic compound containing a nitro group unless there is present in the nucleus some other group such as the amino or the hydroxyl group. Schmitt (Ann. 120, 163), Rose (Zeitschrift f. Chemie 1871, 234), and Meyer (Ann. 165, 164) sulphonated nitrobenzene by warming it with fuming sulphuric acid, stirring constantly until the nitrobenzene was completely dissolved. The reaction was very slow, a day or more being consumed in the process. In a similar manner Beilstein and Kuhlberg (Ann. 155, 18) sulphonated the three nitrotoluenes by treating with four parts of fuming sulphuric acid, stirring and warming. There seems to be no record in the literature of the preparation of the nitrosulphonic acids of metaxylene by sulphonating nitro-m-xylene.

Several attempts to sulphonate the mononitro derivative of p-xylene, using various concentrations of sulphuric acid as an agent, were made. In one experiment 5 c. c. of nitro-p-xylene was treated in the cold with 25 g. of concentrated sulphuric acid. The mixture was allowed to stand at room temperature over night. It was then poured into cold water when the nitro-p-xylene sank to the bottom of the beaker unchanged. A very small amount of solid, which separated out, went into solution on standing.

In a second experiment 5 c. c. of nitro-p-xylene was treated in the cold with 30 g. of concentrated sulphuric acid and allowed to stand over night. It was then heated on the water bath for one hour. 5 c. c. of fuming sulphuric acid (30% anhyd.) was added and the mixture again heated for thirty minutes. When it was poured into cold water, as in the preceding experiment, a considerable amount of nitro-p-xylene separated out. There was also formed a

dark colored precipitate. This was soluble in alcohol and only slightly soluble in ether. It was not studied further.

In a third experiment 5 g. of nitro-p-xylene was treated with 25 g. of concentrated sulphuric acid and at once warmed on the water bath. The reaction was quite violent and although the containing flask was cooled in ice the whole rapidly decomposed to a black spongy mass.

ACTION OF CHLORSULPHONIC ACID ON NITROPARAXYLENE.

In the hope of obtaining a better yield attempts were made to sulphonate nitro-p-xylene by the aid of chlorsulphonic acid. This substance was first used in the sulphonation of aromatic compounds by Knapp (Zeitsh. f. Chemie 1869, 41), who, by means of it, produced from benzene a sulphonchloride, a sulphonic acid and a sulphone. The reaction was later studied by Beckurt and Otto (Ber. 11, 2061) who used it in the production of the sulphonchlorides of toluene, commercial xylene and chlor-benzene. According to these authorities the reaction may take place as designated by any one or all of the following equations:

$$SO_2{<}\begin{matrix}OH\\Cl\end{matrix} + RH = SO_2{<}\begin{matrix}R\\Cl\end{matrix} + H_2O$$

$$SO_2{<}\begin{matrix}OH\\Cl\end{matrix} + RH = SO_2{<}\begin{matrix}OH\\R\end{matrix} + HCl$$

$$SO_2{<}\begin{matrix}OH\\Cl\end{matrix} + 2RH = SO_2{<}\begin{matrix}R\\R\end{matrix} + H_2O + HCl$$

Our knowledge of the reaction, so far as aromatic hydrocarbons are concerned, has been increased by Claesson and Wallin (Ber. 12, 1848), Claesson (Ber. 14, 307),

Limpricht (Ber. 18, 2172) and Pummerer (Ber. 42, 1802; 2274). In general these investigators have shown that aromatic hydrocarbons are acted upon by chlorsulphonic acid at low temperatures to produce mixtures of sulphonchloride, sulphonic acid and sulphone.

Armstrong (Ber. 4, 356) was the first to use the above re-agent in the sulphonation of nitro derivatives of the aromatic hydrocarbons. He treated nitrobenzene, in carbon disulphide solution, with one mol of chlorsulphonic acid obtaining, according to the following probable equation, a sulphonic acid:

$$C_6H_5NO_2+SO_2<\begin{matrix}OH\\Cl\end{matrix}=C_6H_4<\begin{matrix}NO_2\\SO_2OH\end{matrix}+HCl.$$

Later, Dr. F. Von Heyden Nachfolger (D. R. P. 89997; Frdl. 4, 38 (1899)) produced the sulphonchlorides of o-nitrotoluene, p-nitrotoluene and 6-nitro-m-xylene by heating them on the water bath with chlorsulphonic acid. Speaking generally, the nitro derivatives of the aromatic hydrocarbons produce, when heated with two or more mols of chlorsulphonic acid, sulphonchlorides, sulphonic acids and sulphones. If the heating is omitted little, or no, reaction takes place.

From what has been said above, as well as from the fact that Limpricht (Ber. 18, 2172) found that chlorsulphonic acid acts upon the derivatives of aromatic sulphonic acids, such as the amide, to form a sulphonchloride, it appears to the author that the reaction which produces the sulphonchloride takes place in two steps. First, the sulphonic acid is formed as shown in the equation,

$$C_6H_5NO_2+Cl,SO_2OH=C_6H_4(NO_2)SO_2OH+HCl.$$

The nitrosulphonic acid is then acted upon by a second

molecule of chlorsulphonic acid according to the following equation,

$$C_6H_4(NO_2)SO_2OH + Cl,SO_2OH = C_6H_4(NO_2)SO_2Cl + H_2SO_4$$

F. Von Heyden Nachfolger (loc. cit.) found that the $—SO_2Cl$ group took the meta position to the nitro group, there being formed at the same time smaller amounts of the ortho and para compounds.

Of five experiments made, the one with the following proportions of reacting substances and the conditions here described, gave the best results: 100 g. of nitro-p-xylene, which had been purified by two distillations with steam and dried over calcium chloride, was added, drop by drop, to 480 g. of chlorsulphonic acid, surrounded by ice. The dark red mixture, placed in a flask the neck of which was fitted with a calcium chloride tube to protect from atmospheric moisture, was allowed to stand over night. When it was heated on the water bath hydrochloric acid was given off. The heating was continued, with occasional shaking for twelve hours, at the end of which time the evolution of hydrochloric acid gas had practically ceased. When cool the mixture was poured slowly into 2 litres of ice water. This caused the separation of a semi solid brown precipitate which, on standing one hour, solidified in the bottom of the vessel. The solid, which was filtered off and treated with 1 litre of ether, dissolved leaving a small amount of tarry residue. By means of suction, the tarry residue was filtered off from the solution and the latter dried over calcium chloride. After standing two days the addition of 300 c. c. of petroleum ether caused the separation of more tarry matter. After standing five hours longer the solution was filtered free from the tarry matter

and the calcium chloride. 500 c. c. of ether was distilled off and the concentrated solution placed in a beaker where crystals, which tended to adhere to the sides of the beaker, began to form immediately. The evaporation was continued in a current of dry air until the volume of the solution was reduced to 100 c. c. The crystals were filtered off by suction and washed with a mixture of ether and petroleum ether. After recrystallization from ether and petroleum ether they weighed 23 g. One gram of them recrystallized five times from petroleum ether, gave a constant melting point of 74.5°-75.5°. The evaporation of the mother liquor was continued for five days. More crystals separated and at the same time a heavy oil formed in the bottom of the beaker. This second crop of crystals was filtered off and subjected to fractional crystallization. From it was recovered 6.3 g. of the sulphonchloride which melted at 74.5° and 10 g. of the more soluble sulphonchloride, mentioned in previous experiments, melting at 60°. The mother liquor from the second crop of crystals was placed in the ice box and allowed to stand three weeks. It yielded a third crop which weighed 18 g. (crude) and which melted after repeated recrystallizations at 60°. The remaining 10 g. of tarry matter, which probably contained some sulphone and p-xylenesulphonchloride, did not yield crystals when allowed to stand three weeks at low temperature.

In some of the experiments the crude sulphonchloride was recrystallized from pure petroleum ether. While it was more difficultly soluble in the pure petroleum ether than in the mixed solvent, fewer crystallizations were necessary. The tarry impurity, being practically insoluble

in petroleum ether, was left on the sides and bottom of the beaker after the sulphonchloride was dissolved.

One attempt was made to sulphonate nitro-p-xylene in the cold by means of chlorsulphonic acid: 10 g. of nitro-p-xylene was slowly dropped into 60 g. of chlorsulphonic acid, the reacting mixture being cooled in ice. Some hydrochloric acid was given off and, as in the preceding experiment, the solution took on a dark red color. It was placed in a flask, provided with a calcium chloride tube, surrounded with a freezing mixture and allowed to stand over night. When it was poured into water, an oil separated out and the water became rather turbid. The water was poured off and at once extracted with ether. When dried over calcium chloride and evaporated almost to dryness the etherial solution yielded a very small amount (0.25 g.) of the sulphonchloride melting at 74.5°. The oil which settled out when the red solution was poured into water was identified by its odor and boiling point as unchanged nitro-p-xylene.

DETERMINATION OF CONFIGURATION.

In order to determine the configuration of the three crystalline nitrosulphonchlorides, they were hydrolysed to the corresponding sulphonic acids and these were in turn reduced to the corresponding amino acids by means of ammonium sulphide, or stannous chloride and hydrochloric acid. Nolting and Witt (Ber. 18, 2664) isolated a soluble sulphonic acid from the product of the action of concentrated sulphuric acid on commercial xylidine which they determined to be a derivative of p-xylidine. Nolting and Kohn, the following year (Ber. 19, 141), made a more thor-

ough study of this acid. They prepared its barium and sodium salts and assigned to it a formula in which the sulphonic acid group took the para position to the amino group. The assignment of this formula was based upon the results of three experiments. First,—the acid was easily oxidized by means of chromic acid to p-xyloquinone; second,—the sulphonic acid group was displaced when the acid was treated with bromine, a dibromxylidine being formed, and third,—by diazotizing the acid and treating with hydrombromic acid, a brom sulphonic acid of p-xylene was formed that closely resembled in properties an acid which Jacobson prepared by the sulphonation of bromxylene (Ber. 17, 2379). There seems to be no record, however, of the properties of the free acid except that it is readily soluble in fairly concentrated sulphuric acid (Ber. 18, 2664) and that it has an ionization constant of 0.044 (Ostwald, Ph. Ch. 3, 411).

In the article mentioned above, Nolting and Kohn describe a second sulphonic acid of p-xylidine. This they prepared by reducing with ammonium sulphide, or stannous chloride and hydrochloric acid, the crude acid resulting from the nitration of p-xylenesulphonic acid. This amino acid they found to be fairly difficultly soluble in cold water, from which it crystallized in fine white needles containing one molecule of water of crystallization. They produced from this acid, by heating it with nitrobenzene, glycerine and sulphuric acid, a sulphonic acid of quinoline, and for this reason assigned to it a formula in which the sulphonic acid group was given the meta position to the amino group.

Hydrolysis of the Sulphonchloride Which Melted at 60° and Subsequent Reduction of the Acid by Means of Ammonium Sulphide.

5 g. of the soluble nitrosulphonchloride which was formed either by the nitration of p-xylenesulphonic acid and the subsequent treatment of the potassium salt with phosphorous pentachloride, or by the action of chlorsulphonic acid upon nitro-p-xylene, was crystallized three times from a mixture of ether and petroleum ether. It was then placed with 25 c. c. of water in a flask connected with a reflux condenser and boiled for one and one-half hours at the end of which time it was completely decomposed. The solution was decolorized by means of animal charcoal and evaporated on the water bath until crystals began to form. After the solution was dissolved in 50 c. c. of alcohol and saturated with ammonia, a stream of hydrogen sulphide was passed through it for six hours, with occasional warming. The solution darkened in color and considerable sulphur separated out. When it was transferred to a beaker and evaporated on a hot plate, small lustrous needles, together with more sulphur, began to separate almost at once. Evaporation was continued almost to dryness. The residue was acidified with hydrochloric acid, treated with 50 c. c. of water, boiled and filtered free from sulphur. On evaporation of the acidified solution to 25 c. c. the amino acid began to separate slowly in clusters of very fine white needles. It was recrystallized twice from dilute hydrochloric acid and dried between filter papers. Yield, 1.4 g.

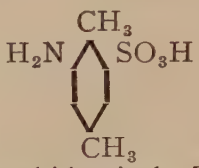
Hydrolysis of the Sulphonchloride Which Melted at 60° and Subsequent Reduction of the Acid by Means of Stannous Chloride and Hydrochloric Acid.

5 g. of the sulphonchloride was recrystallized and hydrolized as in the preceding experiment. After decolorization of the acid solution and evaporation to small bulk it was treated with a little more than three mols (11.5 g.) of crystallized stannous chloride and 6 c. c. of concentrated hydrochloric acid in 15 c. c. of water. When the solution was warmed slightly and allowed to stand over night, needlelike crystals separated out. The mixture was poured into 1500 c. c. of water and heated until the crystals dissolved. Hydrogen sulphide was then passed through the solution until the tin was completely precipitated as sulphides. These were filtered off and the filtrate evaporated on the hot plate to 30 c. c. The amino acid separated as in the preceding experiment. A slightly larger yield was obtained, i. e., 1.8 g.

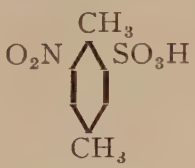
The acid, as prepared by either of the above methods, is quite difficultly soluble in cold water but more readily soluble in hot water. When heated above 200° it begins to char but does not melt when heated as high as 320°. It contains one molecule of water of crystallization which it retains rather persistently, complete dehydration taking place only when the temperature is brought to 160°. An analysis gave the following results:

	Calculated for $C_8H_{11}O_3NS.H_2O$	Found
H_2O	8.21%	8.12%
S	14.6	14.42%

The properties of the above acid resemble very closely those of the aminosulphonic acid of p-xylene, prepared by Nolting and Kohn (Ber. 19, 143), to which they gave the formula



and they are considered identical. The nitrosulphonic acid from which it was prepared must then have the formula,



Hydrolysis of the Sulphonchloride Which Melted at 109.5° and Subsequent Reduction of the Acid by Means of Ammonium Sulphide.

5 g. of the least soluble of the sulphonchlorides, which were formed by the action of phosphorous pentachloride on the crude potassium salts of the acids formed by nitrating p-xylenesulphonic acid, was recrystallized twice from ether to which a little petroleum ether had been added. The resulting clear crystals were boiled with 50 c. c. of water in a reflux condenser for two and one half hours, hydrolysis being complete at the end of this period. The acid solution was evaporated on the hot plate until crystals began to form. This was then dissolved in 50 c. c .of alcohol and saturated with ammonia gas. When a stream of hydrogen sulphide was passed through the solution for three hours, with occasional warming, the color darkened slightly and a very small amount of sulphur separated

out. It was allowed to stand over night and again hydrogen sulphide was passed through it for ten hours with no appreciable change in the appearance of the solution. It was then transferred to a beaker and evaporated to dryness on the water bath. 50 c. c. of water and 5 c. c. of hydrochloric acid was added and the whole boiled. The small amount (0.05 g.) of sulphur was filtered off and the filtrate evaporated to about 4 c. c. On standing two days a few crystals of ammonium chloride separated together with a small number of readily soluble prisms. The whole was redissolved in 10 c. c. of water and boiled with barium carbonate. The undissolved barium carbonate was filtered off and the filtrate evaporated to small bulk. Slightly yellow, translucent crystals separated out which, after one recrystallization, gave the following percentages for water of crystallization and barium:

H_2O	2.82%
Ba	22.25%

These are in close agreement with the theoretical percentages of the barium salt of a nitrosulphonic acid of p-xylene containing one molecule of water of crystallization. It was concluded that the nitrosulphonic acid of p-xylene in question is not reduced by hydrogen sulphide in ammoniacal alcoholic solution. (Note: It will be remembered that Frary was unsuccessful in an attempt to reduce this acid with hydrogen sulphide.)

Hydrolysis of the Sulphonchloride Which Melted at 109.5° and Subsequent Reduction of the Acid by Means of Stannous Chloride and Hydrochloric Acid.

As in the preceding experiment, 5 g. of the crude sulphonchloride was recrystallized from a mixture of ether and petroleum ether and hydrolysed by boiling in a flask connected with a reflux condenser. After evaporation to small bulk the acid solution was treated with a little more than three mols (12 g.) of crystallized stannous chloride, 10 c.c. of concentrated hydrochloric acid and 20 c.c of water. It was warmed for forty-eight hours on the hot plate and diluted to 1800 c.c The tin was precipitated by means of hydrogen sulphide and filtered off leaving a clear solution which was evaporated to small bulk. When the volume reached about 10 c.c. crystals began to form. From this point the evaporation was continued on the water bath almost to dryness, in order to drive off the excess of hydrochloric acid. The residue was dissolved in 25 c. c. of water and boiled with barium carbonate. On filtering off the excess of the latter a considerable amount of p-xylidine was found in the filtrate. This indicated that the p-xylidine sulphonic acid formed was hydrolized, in the presence of the hydrochloric acid, according to the following equation:

$$C_6H_2(\overset{1\text{-}4}{CH_3})_2\overset{2}{NH_2}SO_2OH + H_2O \xrightarrow[(HCl)]{} C_6H_3(\overset{1\text{-}4}{CH_3})_2\overset{2}{NH_2} + H_2SO_4.$$

This view was further borne out by the presence of about 0.3 g. of barium sulphate which settled out when the filtrate was allowed to stand over night. After filtering off the barium sulphate and evaporating to small bulk a few

crystals of the barium salt of the nitrosulphonic acid of p-xylene were recovered together with a little p-xylidine hydrochloride.

It would appear from the results of this experiment that the nitrosulphonic acid, in question, upon being reduced under the conditions given is at once hydrolized to p-xylidine and sulphuric acid. Nolting and Kohn (Ber. 19, 143) mention the occurrence of a small amount of a soluble acid in the mother liquor of the 2-sulpho-6-amino compound of p-xylene which was oxidizable to p-xyloquinone. It is the opinion of the author that their soluble acid (?) was simply the hydrochloride of p-xylidine formed in accordance with the above equation. It has been shown by Rommier (Comp. Rend. 55, 214), Nietzki (Ber. 13, 472) and Nolting (Ber. 18, 2667) that amino derivatives of p-xylene are readily oxidized to the quinone. The author hopes, in the near future, to make a more thorough study of the conduct of this acid toward reducing agents. Simonsen (Trans. 103, 1144) has found that 3-nitro-1,2-Dimethylbenzene-4-sulphonic acid is easily reduced to the amino acid by ferrous sulphate in alkaline solutions.

Hydrolysis of the Sulphonchloride Which Melted at 74.5° and Subsequent Reduction of the Acid by Means of Ammonium Sulphide.

5 g. of the crude sulphonchloride melting at 74.5° after two recrystallizations from a mixture of ether and petroleum ether, was boiled one hour and forty-five minutes with 50 c.c. of water in a flask connected with a reflux condenser. At the end of this time, hydrolysis being complete, the acid solution was decolorized with animal char-

coal and evaporated on the water bath to 5 c.c. 50 c.c. of alcohol was added, the solution saturated with ammonia gas and treated for five hours with hydrogen sulphide as in preceding experiments. The reduction took place readily, the solution became dark in color and a considerable amount of sulphur separated out. Long needles separated from the alcoholic solution when it was cooled. The mixture was evaporated to dryness on a water bath and 5 c.c. of concentrated hydrochloric acid in 100 c.c. of water was added. It was then boiled and the precipitated sulphur was filtered off. On evaporation of the filtrate the aminosulphonic acid came down in clusters of fine prismatic plates or needles which were slightly less soluble than the aminosulphonic acid already described. Yield,—2.6 g.

Hydrolysis of the Sulphonchloride Which Melted at 74.5° and Subsequent Reduction of the Acid by Means of Stannous Chloride and Hydrochloric Acid.

The concentrated solution of nitrosulphonic acid, prepared as in the preceding experiment by the hydrolysis of the sulphonchloride, was treated with 12 g. of stannous chloride and 6 c.c. of concentrated hydrochloric acid in 15 c.c. of water. A precipitate began to form almost at once. The mixture was allowed to stand twenty-four hours and then diluted to 2000 c.c. After precipitating and filtering the tin, in the usual manner, the solution was evaporated. The amino acid came down in the characteristic needlelike plates or prisms as already described. Yield,—3 g.

The sodium salt of the above acid, prepared by neutralizing the acid in solution with sodium hydroxide and evaporating, came down in small soluble white plates containing

no water of crystallization. An analysis yielded the following results:

	Calculated for $C_8H_{10}O_3NSNa$	Found I.	Found II.
Na (as sulphate)	10.32%	10.28%	10.36%

The barium salt, prepared by the barium carbonate method, came down in readily soluble long prismatic plates containing seven molecules of water of crystallization. These lost a part of their water on long exposure to the air, becoming opaque in appearance.

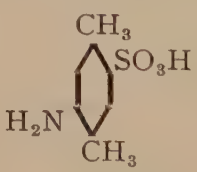
	Calculated for $(C_8H_{10}O_3NS_2)Ba\ 7H_2O$	Found I.	Found II.
H_2O	19.0%	19.12%	19.22%
Ba (as sulphate)	20.7%	20.48%	20.36%

The above described sodium and barium salts are identical in properties with the same salts of the 5-amino-2-sulphonic acids of p-xylene described by Nolting and Kohn (Ber. 19, 141). As previously stated, however, the free acid is described only as being soluble in sulphuric acid. In order to obtain a better comparison the 5-amino-2-sulphonic acid was prepared by the following method: 10 g. of p-xylidine was treated with 9 g. of concentrated sulphuric acid and the mixture heated six hours at a temperature of 220°. After cooling the mass was placed in 1000 c.c. of water, boiled for ten minutes and the solution filtered free from charred matter. It was then neutralized with barium carbonate the excess of the latter being filtered off. On evaporation the barium salt came down in the characteristic soluble prismatic plates some of which were more than three centimeters in length. After drying be-

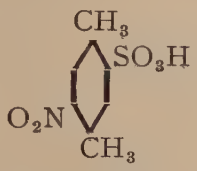
tween filter paper 3.2 g. of this salt was dissolved in 400 c.c. of water, treated with the calculated amount (2.45 c.c.) of ten per cent sulphuric acid and digested on the hot plate for one hour. The barium sulphate was filtered off and the solution evaporated to 100 c.c. The acid came down in well formed colorless needlelike plates which resembled closely in appearance those formed by the reduction of the nitrosulphonic acid formed by the hydrolysis of the sulphonchloride melting at 74.5°.

In order to further verify the identity of the acids, the one resulting from the reduction of the nitrosulphonic acid was subjected to oxidation with chromic acid as follows: 1 g. of the acid was dissolved in a mixture of 10 c.c. of concentrated sulphuric acid and 30 c.c. of water. The solution was cooled and 1 g. of finely ground potassium dichromate was added to it in small portions. It was allowed to stand over night and then treated with 2 g. more of the dichromate. After standing twenty-four hours the dark colored solution was extracted with ether. The etherial solution yielded, on evaporation, 0.54 g. of p-xyloquinone (Phlorone) which came down in yellow needles and melted, after two recrystallizations from benzene, at 124°—124.5°.

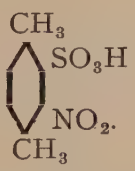
The acid is, then, identical with the one prepared by Nolting and Kohn (Ber. 19, 141) by the sulphonation of p-xylidine and must have the following formula



The acid from which it was formed by reduction must then have the formula

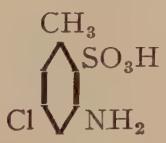


Since the nitrosulphonchloride melting at 60° yields on hydrolysis the 6-nitro-1, 4-dimethylbenzene-2-sulphonic acid, and since the nitrosulphonchloride melting at 74.5° yields on the same treatment the 5-nitro-1, 4-dimethylbenzene-2-sulphonic acid, it follows that the nitrosulphonchloride melting at 109.5° must yield on hydrolysis a nitrosulphonic acid in which the nitro and sulpho groups occupy the ortho position relative to each other. In other words it must yield the 3-nitro-1, 4-dimethylbenzene-2-sulphonic acid,



The fact that the acid was not reduced by hydrogen sulphide in ammoniacal alcoholic solution favors this formula since the protective influences of two groups ortho to the nitro group would naturally be great. It is further shown (pg. 49) that the phenyl ester is produced more slowly from the nitrosulphonchloride melting at 109.5° than from either of the other nitrosulphonchlorides. The retarding of the reaction was probably due to the same protective influence of the two ortho groups. Finally, the very fact that the amino sulphonic acid which is formed by reducing

this acid with stannous chloride and hydrochloric acid is readily hydrolized in the presence of acids to p-xylidine, favors the assigned formula. Traube (Ber. 26,579) has shown that the Chloraminotoluenesulphonic acid, of the formula



is readily hydrolized in acid solution to the corresponding chloraminotoluene. It is readily seen that the relative position of the mehtyl, sulpho, and amino groups is the same in both acids.

SEPARATION OF THE NITRATION PRODUCTS OF PARAXYLENESULPHONIC ACID BY MEANS OF THE BARIUM SALTS.

In the hope of obtaining a larger yield of the acids produced by the nitration of p-xylenesulphonic acid, the following experiment was carried out; 10 g. of the dry p-xylenesulphonic acid was nitrated in the cold with a mixture of 14 g. of nitric acid (sp. gr. 1.51) and 8 g. of concentrated sulphuric acid. After all of the acid had been added and the violence of the reaction had abated, the mixture was heated two hours on the water bath to drive off the nitric fumes. The resulting syrup was heated one hour on the sand bath at 125°, diluted to 300 c.c., treated with barium carbonate and boiled. The excess of barium carbonate was filtered off and the solution was evaporated to 25 c.c. Crystals formed which had a tendency to cling to the sides of the beaker. The solution was cooled and

the crystals were filtered off. When dried between filter papers they weighed 5.5 g. The mother liquor was evaporated to 10 c.c. and cooled. The second crop of crystals which formed was filtered off by suction, washed and dried between filter paper. Yield,—4.2 g.

In order to identify the salts they were converted into the sulphonchlorides and these were identified by means of their melting points. Descriptions of the operations and results are given here.

The first crop of crystals was dried at 110° and treated with 9 g. of phosphorous pentachloride. A small amount of phosphorous oxychloride was added to start the reaction and the mixture was heated two hours on the water bath. The resulting syrup, when poured into water and allowed to stand two hours, solidified. It was filtered off, dissolved in ether and dried over calcium chloride. On evaporation of the etherial solution 1.1 g. of the sulphonchloride melting at 60° separated out. A very few crystals of the sulphonchloride melting at 74.5° came down with those melting at 60° and were separated from them mechanically.

The more soluble barium salt was dried and treated with 6 g. of phosphorous pentachloride. On duplicating the operations of the above experiment, 0.9 g. of the sulphonchloride melting at 109.5° together with a small amount of oil which failed to solidify, was obtained. This last was identified by means of its amide as the sulphonchloride of p-xylene.

From the above it is evident that a better yield of the nitrosulphonic acids may be obtained when they are separated by means of their barium salts than can be obtained by converting them to the sulphonchlorides. Especially is

this true of the 6-nitro-2-sulpho compound which was obtained in a somewhat larger amount than the 3-nitro-2-sulpho compound. The author is inclined to believe that a considerable amount of the first named was not recovered in the form of its chloride because of the solubility of this compound and its extreme slowness of crystallization.

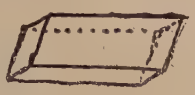
PREPARATION OF NEW COMPOUNDS AND DESCRIPTION OF THEIR PROPERTIES.

A large quantity of each of the three nitrosulphonchlorides of p-xylene was prepared as described in the foregoing methods, and these were used as the starting points in the preparation of a large number of derivatives. These derivatives include the free acids, the amides, the anilides, the phenyl esters, and the sodium, potassium, calcium, barium and silver salts. All of the above are here described and, in addition, the barium salt of the 6-amino-1, 4-dimethylbenzene-2-sulphonic acid. A more complete description of the 5-amino-1, 4-dimethylbenzene-2-sulphonic acid than is found in the literature is also given.

Derivatives of 6-Nitro-1,4-dimethylbenzene-2-sulphonic Acid.

The **Sulphonchloride,** $C_6H_2(CH_3)_2.NO_2SO_2Cl$. The sulphonchloride of the acid was formed in two ways, first, by the action of phosphorous pentachloride on the crude potassium salts of the acids formed by nitrating p-xylene-sulphonic acid and second, by the action of chlorsulphonic acid on nitro-p-xylene. Since it is more soluble than either

of the other nitrosulphonchlorides it came down, after these had separated out, from a mixture of ether and petroleum ether. It forms regular rhombohedral prisms as represented in the diagram.



They tend to a slight amber shade even after repeated crystallizations and show a decided tendency to form clusters. The chloride is readily soluble in ether, chloroform, carbon tetrachloride, benzene and carbon disulphide. It is less soluble in petroleum ether. When dissolved in a mixture of ether and petroleum ether it tends to settle out as a heavy oil on evaporation of the solution at ordinary temperatures. It is best crystallized from this mixed solvent at a temperature of about 10°. It melts to an oil under hot water by which it is slowly hydrolized to the acid. Melting point, 60°—61°.

	Calculated for $C_8H_8O_4NSCl$	Found I.	Found II.
Cl	14.2%	14.26%	14.3%
S	12.82%	12.66%	.....
N	5.61%	5.54%	5.48%

1-4 6 2

The Acid, $C_6H_2(CH_3)_2.NO_2.SO_2OH.H_2O$. This was formed by the hydrolysis of the sulphonchloride just described: 10 g. of the sulphonchloride was boiled one and one-half hours with 150 c.c. of water in a flask connected with a reflux condenser. At the end of this time, hydrolysis being complete, the solution was decolorized by boiling with animal charcoal and evaporated on the water bath

to a thick syrup. On cooling the acid crystallized out in plates. It was filtered off by suction, washed twice with concentrated hydrochloric acid in which it is rather insoluble, and dried over sodium hydroxide. 6-nitro-1,4-dimethylbenzene-2-sulphonic acid has a bitter taste. It is so extremely hygroscopic that it dissolves on standing in the air in the water absorbed by it. It is soluble in alcohol but decidedly insoluble in ether, chloroform, carbon tetrachloride, benzene and carbon disulphide. When dried over sodium hydroxide and heated to 128° it begins to char but does not melt when heated to 200°. It contains one molecule of water of crystallization which it loses readily at 100°.

	Calculated for $C_8H_9O_5NS.H_2O$	Found I.	II.
H_2O	7.23%	7.04%	7.15%
Acid hydrogen	.401%	.392%	.....
N	5.62%	5.66%	5.58%

1-4 6 2.

The Amide, $C_6H_2(CH_3)_2\ NO_2\ SO_2NH_2$. 1 g. of the sulphonchloride was treated with 5 c.c. of concentrated ammonium hydroxide and heated on the hot plate. The sulphonchloride melted to an oil which was soon decomposed, a flocculent precipitate being formed. The mixture was evaporated almost to dryness and the residue washed repeatedly with water. It was then dissolved in 25 c.c. of alcohol. An equal volume of water was added and the solution set aside to crystallize. The amide of 6-nitro-1, 4-dimethylbenzene-2-sulphonic acid comes down in clusters of very fine prismatic plates which are readily soluble in alcohol, ether and chloroform but insoluble in

water. After repeated recrystallization from fifty per cent alcohol it has a constant melting point of 172°—173°.

	Calculated for $C_8H_{10}O_4N_2S$	Found I.	Found II.
S	13.91%	13.84%	.....
N	12.17%	11.81%	12.16%

1-4 6 2

The Anilide, $C_6H_2(CH_3)_2\,NO_2\,SO_2HNC_6H_5$. 1 gr. of the sulphonchloride was dissolved in 5 c.c. of carbon tetrachloride and treated with excess of aniline. A precipitate settled at once. The solvent was evaporated on the hot plate and the residue washed three times with hydrochloric acid (1:1). It was then dissolved in ten per cent sodium hydroxide solution, cooled and reprecipitated with hydrochloric acid. The anilide was filtered off and recrystallized three times from fifty per cent alcohol. It comes down in clusters of fine, hard, flat needles which are readily soluble in hot alcohol, less soluble in cold, fairly soluble in ether, chloroform and carbontetrachloride, but insoluble in water. It melts, after three recrystallizations from fifty per cent alcohol, at 143°—144°.

	Calculated for $C_{14}H_{14}O_4N_2S$	Found
S	10.46%	10.44%
N	9.07%	9.05%

1-4 6 2

The Phenyl Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_5$. Three methods were used in preparing this ester, towit, the Schotten-Baumann method, the pyridine method of Reverdin (Ber. 35, 1443) and a method in which the sulphonchloride was treated with sodium phenolate in benzene solution.

Schotten and Baumann Method.

2 g. of the sulphonchloride was added in small portions, with constant shaking, to 200 c.c. of an alkaline solution of sodium phenolate. (Note,—Prepared by dissolving 6 g. of phenol and 3.2 g. of sodium hydroxide in enough water to make 200 c.c.) The chloride gradually disappeared and a light colored pasty mass separated out. After five hours the supernatant liquid was poured off. The residue was washed twice with water, dissolved in alcohol and the solution evaporated to crystallization. The ester came down in nodules of very fine plates. Yield,—70% of theory.

Reverdin Method.

1 g. of phenol was mixed with an equal weight of pyridine and to this mixture was added 2.65 g. of the sulphonchloride. This dissolved with evolution of heat. The solution was warmed on the water bath for five minutes. On cooling it solidified to a granular mass which was washed twice with water and dissolved in hot alcohol. The ester came down in the form described in the previous experiment. Yield,—88% of theory.

Sodium Phenolate—Benzene Method.

5 g. of phenol was dissolved in 25 c. c. of benzene and to this solution was added 0.8 g. of metallic sodium. After standing three hours this mixture was treated with 2 g. of the sulphonchloride. Heat was evolved and both the sulphonchloride and the sodium phenolate dissolved while sodium chloride precipitated out. After twenty-four hours 50 c. c. of water was added and the mixture

heated on the hot plate until most of the benzene had been driven off. The resulting semisolid mass was washed repeatedly with water and allowed to stand forty-eight hours when it solidified. It was dissolved in hot alcohol and the solution evaporated to crystallization. Yield,—75% of theory.

It is evident that the Reverdin method is shorter and gives a better yield than either of the others tried. It was therefore adopted in the preparation of the other phenyl esters.

The phenyl ester of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid crystallizes from alcoholic solution in clusters of fine needlelike plates which have a constant melting point of 117°-118°. It is fairly readily soluble in chloroform, carbon tetrachloride and benzene, but insoluble in water.

	Calculated for $C_{14}H_{13}O_5NS$	Found I.	Found II.
S	10.4%	10.18%	10.29%
N	4.56%	4.53%	.....

Sodium Salt, $C_6H_2(CH_3)_2NO_2SO_3Na.2H_2O$. In order to prepare this salt a solution of the sulphonic acid, produced by the hydrolysis of the nitrosulphonchloride melting at 60°, was just neutralized with a ten per cent solution of sodium hydroxide (Litmus). The solution was decolorized with animal charcoal, filtered and evaporated to small bulk. The sodium salt comes down in treelike clusters of very soluble prismatic plates. It is readily soluble in hot alcohol and less soluble in cold. It contains two molecules of water of crystallization which it loses

when heated six hours at 108°. This salt may also be prepared by treating a concentrated solution of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid with a saturated solution of sodium chloride.

	Calculated for $C_8H_8O_5NSNa.2H_2O$	Found
H_2O	12.8%	12.69%
Na (as sulphate)	7.96%	7.79%

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$. A solution of the 6-nitro-1,4-dimethylbenzene-2-sulphonic acid was exactly neutralized with a ten per cent solution of potassium hydroxide, litmus being used as an indicator. The solution was decolorized with animal charcoal and evaporated to small bulk. On standing the potassium salt came down in clusters or rosettes of readily soluble, colorless, prismatic plates containing one molecule of water of crystallization. It is slightly less soluble in alcohol than the sodium salt. It is precipitated from concentrated solution on the addition of strong potassium hydroxide solution or a saturated solution of potassium chloride. This salt is more readily precipitated from a concentrated solution of the sulphonic acid on addition of potassium chloride than is the corresponding sodium salt on addition of sodium chloride.

	Calculated for $C_8H_8O_5NSK.H_2O$	Found
H_2O	6.24%	6.34%
K (as sulphate)	14.53%	14.26%

Calcium Salt, $(C_6H_2(CH_3)_2NO_2SO_3)_2Ca.4H_2O$. A solution of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid was boiled with precipitated calcium carbonate. The excess of calcium carbonate was filtered off and the solution evaporated. The salt came down in treelike clusters of colorless crystals. It is less soluble than the calcium salt of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid and slightly more soluble than that of 5-nitro-1,4-dimethylbenzene-2-sulphonic acid. It is slightly soluble in alcohol. This salt retains its water of crystallization rather persistently, it being necessary to heat it ten hours at 200° to effect complete dehydration.

	Calculated for $(C_8H_8O_5NS)_2Ca.4H_2O$	Found
H_2O	12.58%	12,45%
Ca (as sulphate)	7.01%	6.97%

Barium Salt, $(C_6H_2(CH_3)_2NO_2SO_3)_2Ba.2H_2O$. This salt was prepared from a solution of the nitrosulphonic acid and barium carbonate after the same manner as the calcium salt. It came down in small colorless nodules which showed a tendency to adhere to the sides of the beaker. It is slightly soluble in hot alcohol and less soluble in cold. It loses one of its two molecules of water of crystallization when heated four hours at 150°. A temperature of 200° for six hours is necessary to drive off the second molecule.

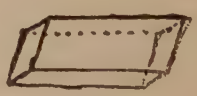
	Calculated for $(C_8H_8O_5NS)_2Ba.2H_2O$	Found
H_2O	5.68%	5.67%
Ba (as sulphate)	21.69%	21.71%

Silver Salt, $C_6H_2(^{1-4}CH_3)_2{}^{6}NO_2{}^{2}SO_3Ag.H_2O$. The nitrosulphonic acid in solution was treated with a little more than the calculated amount of silver nitrate and boiled. The small amount of silver chloride was filtered off and the solution evaporated. The silver salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid comes down in clusters of fine needlelike plates containing one molecule of water of crystallization. It is less soluble than the silver salt of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid and slightly more soluble than the silver salt of 5-nitro-1,4-dimethylbenzene-2-sulphonic acid. It is very slightly soluble in alcohol. When exposed to the light the crystals slowly decompose and darken in color. They lose their water of crystallization readily when heated above 100°.

	Calculated for $C_8H_8O_5NSAg.H_2O$	Found
H_2O	5.07%	4.91%
Ag (as metal)	30.39%	30.43%

Derivatives of 3-Nitro-1,4-dimethylbenzene-2-sulphonic Acid.

The Sulphonchloride, $C_6H_2(^{1-4}CH_3)_2{}^{3}NO_2{}^{2}SO_2Cl$. This compound is formed, together with the 6-nitro-1,4-dimethylbenzene-2-sulphonchloride when the crude potassium salts of the acids formed by nitrating p-xylenesulphonic acid, are treated with phosphorous pentachloride. It is less soluble in a mixture of ether and petroleum ether than the 6-nitro-1,4-dimethylbenzene-2-sulphonchloride and is separated from it by fractional crystallization. It crystallizes out in clear rombohedral prisms,



which have a constant melting point of 109.5°. It is readily soluble in ether, chloroform, carbo ntetrachloride and benzene but less soluble in these than the nitrosulphonchloride which is formed with it. It is less soluble in petroleum ether than in other organic solvents. It is slowly decomposed when boiled with water but it does not melt to an oil under the water.

	Calculated for $C_8H_8O_4NSCl$	Found I.	Found II.
Cl	14.2 %	14.32%	14.26%
S	12.82%	12.81%	12.72%
N	5.61%	5.66%	.....

The Acid, $C_6H_2(CH_3)_2NO_2SO_2OH.H_2O$ (1-4 3 2). The 3-nitro-1,4-dimethylbenzene-2-sulphonic acid was prepared by boiling 10 g. of its sulphonchloride with 150 c. c. of water three hours and twenty minutes in a flask connected with a reflux condenser. On evaporating the solution to a syrup and cooling the acid crystallized in clusters of elongated plates. These were filtered off by suction, washed twice with concentrated hydrochloric acid and dried over sodium hydroxide. The acid contains one molecule of water of crystallization in which it melts when heated to 100°. When heated twenty-four hours at 108° it first melts and then slowly hardens and becomes crystalline. When thus dehydrated the acid melts between 143° and 145° with partial decomposition. Like the 6-nitro-1,4-dimethylbenzene-2-sulphonic acid it is less soluble in concentrated hydrochloric acid than in water, fairly readily soluble in alcohol, but insoluble in ether, chloroform, carbon tetrachloride, carbon disulphide, benzene and petro-

leum ether. It dissolves, on standing in the air, in the water it absorbs.

	Calculated for $C_8H_9O_5NS.H_2O$	Found
H_2O	7.23 %	7.08 %
Acid hydrogen	.401%	.396%
N	5.62 %	5.57 %

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$. 1 g. of 3-nitro-1,4-dimethylbenzene-2-sulphonchloride was treated with an excess of concentrated ammonium hydroxide, warmed and allowed to stand over night. As this treatment did not decompose the crystals the mixture was heated three hours on the hot plate and at the end of this time solution was complete. On evaporation the amide came down in fine flat shiny needles which, after repeated crystallization from fifty per cent alcohol, melted at 191°-192°. This amide closely resembles that of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid in its solubilities.

	Calculated for $C_8H_{10}O_4N_2S$	Found I.	Found II.
S	13.91%	13.8 %	13.86%
N	12.17%	12.21%	.....

The Anilide, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_5$. This compound was prepared from the 3-nitro-1,4-dimethylbenzene-2-sulphonchloride by treating the latter in carbon tetrachloride solution with excess of aniline. The details of the experiment were exactly the same as those described for the preparation of the anilide of the 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. 3-nitro-1,4-dimethyl-

benzene-2-sulphonanilide crystallizes from fifty per cent alcohol in long flat needles having characteristic ends, . It has a constant melting point of 181.5°-182.5°. It is insoluble in water and slightly less soluble in organic solvents than the anilide of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. The crystals retain a slight bluish tinge after ten recrystallizations.

	Calculated for $C_{14}H_{14}O_4N_2S$	Found
S	10.46%	10.37%
N	9.07%	9.06%

The Phenyl Ester, $C_6H_2(^{1\text{-}4}CH_3)_2{}^{3}N{}^{2}O_2SO_3C_6H_5$. The pyridine method of Reverdin, already described, was used in the preparation of this ester. The 3-nitro-1,4-dimethylbenzene-2-sulphonchloride dissolved more slowly in the pyridine-phenol mixture than did the 6-nitro-1,4-dimethylbenzene-2-sulphonchloride, solution being complete after the mixture had been heated fifteen minutes on the water bath. After cooling and washing the ester was recrystallized from alcohol in the usual manner. It comes down in well formed colorless prisms which show a slight tendency to adhere to the sides of the beaker. After one recrystallization it has a constant melting point of 83°-83.5°. This ester closely resembles the phenyl ester of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid as regards its action toward solvents.

	Calculated for $C_{14}H_{13}O_5NS$	Found
S	10.4 %	10.47%
N	4.56%	4.51%

Sodium Salt, $C_6H_2(^{1-4}CH_3)_2{}^{3}NO_2{}^{2}SO_3Na.2H_2O$. This salt was prepared by exactly neutralizing a solution of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid with ten per cent sodium hydroxide solution using litmus as an indicator. The solution was decolorized, filtered and evaporated to small bulk. The salt came down in clusters of small light yellow prismatic plates. Its solubility in water and in alcohol resembles that of the sodium salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. Like this last named compound it is easily prepared by treating a concentrated solution of the acid with saturated sodium chloride solution It loses its water of crystallization when heated six hours at 108°.

	Calculated for $C_8H_8O_5NSNa.2H_2O$	Found
H_2O	12.8 %	12.68%
Na	7.96%	7.98%

Potassium Salt, $C_6H_2(^{1-4}CH_3)_2{}^{3}NO_2{}^{2}SO_3K.H_2O$. The potassium salt of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid was prepared by a method identical with the one used in preparing the potassium salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. It comes down in tufts of colorless needlelike plates which are slightly less soluble than the crystals of the corresponding sodium salt. The solubility of this salt in water and alcohol is about the same as that of the potassium salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. It contains one molecule of water of

crystallization which it retains rather persistently, a temperature of 200° being required for complete dehydration.

	Calculated for $C_8H_8O_5NSK.H_2O$	Found I.	Found II.
H_2O	6.24%	6.02%	.....
K	14.53%	14.18%	14.36%

Calcium Salt, $(C_6H_2(CH_3)_2NO_2SO_3)_2Ca.3H_2O$. This salt was prepared by boiling a solution of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid with precipitated calcium carbonate, filtering off the excess and evaporating. It comes down in slightly yellow, translucent irregular crystals. It is more soluble than the calcium salts of either of the isomeric acids and than the barium salt of this same acid. It is only fairly soluble in alcohol. One of its three molecules of water of crystallization is given off when it is heated three hours at 108°. A temperature of 200° for eight hours is necessary for complete dehydration.

	Calculated for $(C_8H_8O_5NS)_2Ca.3H_2O$	Found
H_2O	9.74%	9.87%
Ca	7.24%	7.26%

Barium Salt, $(C_6H_2(CH_3)_2NO_2SO_3)_2Ba.H_2O$. This salt was prepared from the 3-nitro-1,4-dimethylbenzene-2-sulphonic acid and barium carbonate in the same manner as the barium salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. It comes down in irregular translucent crystals which resemble closely in appearance those of the calcium salt of the acid under consideration. It is more soluble than the barium salts of the isomeric acids. Its solu-

bility in alcohol is about the same as the barium salt of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid. It loses its water of crystallization when heated eight hours at 200°.

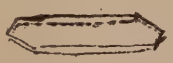
	Calculated for $(C_8H_8O_5NS)_2Ba.H_2O$	Found
H_2O	2.92%	2.84%
Ba	22.32%	22.22%

Silver Salt, $C_6H_2(^{1-4}CH_3)_2{}^{3}NO_2{}^{2}SO_3Ag.H_2O$. 3-nitro-1,4-dimethylbenzene-2-sulphonic acid was treated with a little more than the calculated amount of silver nitrate, boiled and filtered free from silver chloride. The silver salt came down from the concentrated solution in readily soluble plates. It is slightly soluble in alcohol. When exposed to light it darkens more readily than either of the other silver salts. It loses its water of crystallization readily when heated to 108°.

	Calculated for $C_8H_8O_5NSAg.H_2O$	Found I.	II.
H_2O	5.07%	5.05%	5.12%
Ag	30.39%	(puffed)	30.44%

Derivatives of 5-Nitro-1,4-Dimethylbenzene-2-sulphonic Acid.

The Sulphonchloride, $C_6H_2(^{1-4}CH_3)_2{}^{5}NO_2{}^{2}SO_2Cl$. This sulphonchloride was formed, together with about an equal amount of the sulphonchloride of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid, when nitro-p-xylene was heated with an excess of chlorsulphonic acid. After the reacting mixture had been poured into ice water the resulting semi-

solid matter was dissolved in ether and dried over calcium chloride. Most of a tarry impurity was precipitated out by the addition of petroleum ether and this, together with the calcium chloride, was filtered off. On evaporation of the solution the sulphonchloride separated out, together with some of the more soluble 6-nitro-1,4-dimethylbenzene-2-sulphonchloride from which it was separated by fractional crystallization. 5-nitro-1,4-dimethylbenzene-2-sulphonchloride precipitates in small crystals which show a tendency to adhere to the sides of the beaker. On repeated recrystallization from ether or from a mixture of ether and petroleum ether the crystals take the form of colorless plates with slightly thickened centres and characteristic ends,  . It is readily soluble in ether, chloroform, carbon tetrachloride, carbon disulphide, and benzene but less soluble in petroleum ether. Its solubility in the above solvents seems to be about the same as that of the sulphonchloride of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid. It melts to an oil under hot water by which it is decomposed. The pure sulphonchloride melts at 74.5°-75.5°.

	Calculated for $C_8H_8O_4NSCl$	Found I.	Found II.
Cl	14.2 %	14.29%	.....
S	12.82%	12.8 %	13.03%
N	5.61%	5.64%	5.68%

The Acid, $C_6H_2(^{1}CH_3)_2(^{4}NO_2)(^{5}SO_2OH),H_2O$. 5-nitro-1,4-dimethylbenzene-2-sulphonic acid was prepared by hydrolizing the corresponding sulphonchloride in the manner already described. The time necessary for hydrolysis of

10 g. was two hours and ten minutes. The acid comes down in clusters of needlelike plates from the concentrated solution. It is slightly less soluble than its isomers in water and much less soluble in concentrated hydrochloric acid. It is readily precipitated from concentrated aqueous solution by adding an equal volume of concentrated hydrochloric acid and cooling. When recrystallized three times from hydrochloric acid and dried over sodium hydroxide it melts with partial decomposition between 138° and 140°. Like the other acids described it is extremely hygroscopic, has a bitter taste and is insoluble in all of the organic solvents tried except alcohol. It loses its water of crystallization when heated at 108°.

	Calculated for $C_8H_9O_5NS.H_2O$	Found I.	Found II.
H_2O	7.23 %	7.22 %	.....
Acid hydrogen	.401%	.394%	.....
N	5.62 %	5.49 %	5.56%

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$. 1 g. of the 5-nitro-1,4-dimethylbenzene-2-sulphonchloride was decomposed with excess of ammonium hydroxide and the mixture evaporated almost to dryness on the hot plate. The residue was washed repeatedly with water and dissolved in fifty per cent alcohol. On evaporation the amide came down in fine prismatic plates which may or may not form clusters. When heated the crystals become opaque at about 170° and melt at 197°-198°.

	Calculated for $C_8H_{10}O_4N_2S$	Found
S	13.91%	13.96%
N	12.17%	12.18%

The Anilide, $C_6H_2(^{1-4}CH_3)_2{}^{5}NO_2{}^{2}SO_2HNC_6H_5$. This compound was prepared in the same manner as the anilides already described. It crystallizes out of fifty per cent alcohol, in which it is slightly less soluble than its isomers, in clusters of fine prismatic plates. After three recrystallizations it has a constant melting point of 130.5°-131°.

	Calculated for $C_{14}H_{14}O_4N_2S$	Found I.	II.
S	10.46%	10.36%	10.42%
N	9.07%	9.02%	.....

The Phenyl Ester, $C_6H_2(^{1-4}CH_3)_2{}^{5}NO_2{}^{2}SO_3C_6H_5$. This ester was prepared by the Reverdin method. The sulphonchloride passed into solution immediately with evolution of heat. The ester comes down from alcoholic solution in clusters of light yellow needlelike plates, having a constant melting point of 120°-120.5°.

	Calculated for $C_{14}H_{13}O_5NS$	Found I.	II.
S	10.4 %	10.47%	.....
N	4.56%	4.49%	4.61%

Sodium Salt, $C_6H_2(^{1-4}CH_3)_2{}^{5}NO_2{}^{2}SO_3Na.H_2O$. This salt was prepared in the same manner as the sodium salts of the isomeric acids. It comes down in clusters of flat colorless needles. It is less soluble in water than either of the other sodium salts and rather sparingly soluble in alcohol. It gives up its water of crystallization readily at 108°.

	Calculated for $C_8H_8O_5NSNa.H_2O$	Found
H_2O	6.64%	6.75%
Na	8.48%	8.33%

Potassium Salt, $C_6H_2(^{1}CH_3)_2(^{4}NO_2)(^{5}SO_3)(^{2}K).H_2O$. Prepared in the usual manner, this salt comes down in clusters of shining colorless needlelike plates. It is the least soluble in water and alcohol of any of the sodium or potassium salts studied. It is completely dehydrated when heated six hours at 108°.

	Calculated for $C_8H_8O_5NSK.H_2O$	Found I.	Found II.
H_2O	6.24%	6.36%	6.21%
K	14.53%	14.12% (puffed)	14.45%

Calcium Salt, $(C_6H_2(^{1}CH_3)_2(^{4}NO_2)(^{5}SO_3)(^{2}))_2Ca.3H_2O$. This salt was prepared in the usual manner from calcium carbonate and a solution of 5-nitro-1,4-dimethylbenzene-2-sulphonic acid. It is the least soluble of the calcium salts studied. It comes down from aqueous solution in tufts of long flat colorless needles which are very sparingly soluble in alcohol. It loses one of its three molecules of water of crystallization when heated four hours at 108°. A temperature of 200° for ten hours is required for complete dehydration.

	Calculated for $(C_8H_8O_5NS)_2Ca.3H_2O$	Found
H_2O	9.74%	9.57%
Ca	7.24%	7.16%

Barium Salt, $(C_6H_2(^{1}CH_3)_2(^{4}NO_2)(^{5}SO_3)(^{2}))_2Ba.2H_2O$. This is the least soluble of the barium salts of the nitrosulphonic acids of p-xylene. It comes down in tufts of very fine. colorless needles which show a tendency to adhere to the

sides of the beaker. Its solubility in alcohol is about the same as that of the calcium salt of the same acid. It is dehydrated when heated six hours at 200°.

	Calculated for $(C_8H_8O_5NS)_2Ba.2H_2O$	Found
H_2O	5.68%	5.56%
Ba	21.69%	21.73%

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$ (1-4 5 2). 1 g. of the 5-nitro-1,4-dimethylbenzene-2-sulphonic acid, in concentrated solution, was treated with about one and one-fourth mols of silver nitrate in 5 c. c. of water. The silver salt of the acid precipitated out at once, together with some silver chloride, as a spongy mass. On diluting to 75 c. c. and boiling all but the silver chloride went into solution. This last was filtered off and the filtrate evaporated to 30 c. c. On cooling the silver salt came down in clusters of long, shining needles. It is considerably less soluble than either of the other silver salts studied and darkens when exposed to the light more slowly than these.

	Calculated for $C_8H_8O_5NSAg.H_2O$	Found
H_2O	5.07%	4.95%
Ag	30.39%	30.29%

All of the salts of the three nitrosulphonic acids of p-xylene which were studied are insoluble in ether, chloroform, carbon tetrachloride, carbon disulphide, benzene and petroleum ether.

5-Amino-1,4-dimethylbenzene-2-sulphonic Acid,

$$C_6H_2(\overset{1\text{-}4}{CH_3})_2\overset{5}{N}H_2\overset{2}{SO_3}H$$

As has already been stated, the barium and sodium salts of this acid have been studied but there is very little in the literature concerning the properties of the acid itself. As prepared by the reduction of the corresponding nitro-sulphonic acid, or by the sulphonation of p-xylidine and subsequent purification by means of the barium salt, the acid comes down in clusters of fine prismatic plates or needles. It is somewhat less soluble in water and dilute acids than the 6-amino-1,4-dimethylbenzene-2-sulphonic acid described by Nolting and Kohn (Ber. 19, 143). It is quite readily soluble in fairly concentrated sulphuric acid. It contains no water of crystallization. When heated above 230° it begins to char but does not melt when heated as high as 300°.

	Calculated for	Found	
	$C_8H_{11}O_3NS$	I.	II.
S	15.91%	15.62%	15.74%

The Barium Salt of 6-Amino-1,4-dimethylbenzene-2-sulphonic Acid,

$$(C_6H_2(\overset{1\text{-}4}{CH_3})_2\overset{6}{N}H_2\overset{2}{SO_3})_2Ba.7H_2O$$

The amino-sulphonic acid prepared by reducing 6-nitro-1,4-dimethylbenzene-2-sulphonic acid was dissolved in hot water and neutralized with barium carbonate. The excess of the latter was filtered off and the filtrate evaporated to small bulk. The barium salt comes down in plates which resemble closely in appearance the barium

salt of 5-amino-1,4-dimethylbenzene-2-sulphonic acid. They are, however, slightly more soluble. The salt contains seven molecules of water of crystallization which it loses readily when heated to 108°.

	Calculated for $(C_8H_{10}O_3NS)_2Ba.7H_2O$	Found I.	Found II.
H_2O	19. %	19.28%	19.18%
Ba	20.7%	20.52%	20.61%

SUMMARY AND DISCUSSION.

1. Nitric acid acts upon the sulphonic acid of p-xylene to produce three nitrosulphonic acids. The 6-nitro-1,4-dimethylbenzene-2-sulphonic acid and the 3-nitro-1,4-dimethylbenzene-2-sulphonic acid are produced in fairly good yields and in about equal amounts while the 5-nitro-1,4-dimethylbenzene-2-sulphonic acid is produced in very small amounts. It has been shown by Nolting and Geissmann (Ber. 19, 144), Lellman (Ann. 228, 250) and others that concentrated nitric acid when warmed with p-xylene produces, in the main, the 2-6 and the 2-3-dinitro-p-xylenes with a very small amount of 2-5-dinitro-p-xylene. It would seem, therefore, that the entering nitro group tends to take the meta or the ortho position to the sulphonic acid group just as a second nitro group tends to take the meta or ortho position to the first nitro group.

2. The nitrosulphonic acids of p-xylene, produced by the nitration of p-xylenesulphonic acid, are best separated by converting them into the sulphonchlorides and crystallizing the latter from a mixture of ether and petroleum ether. One separation was made by fractional crystallization of the barium salts. This method gave a somewhat

larger yield of the 6-nitro-1,4-dimethylbenzene-2-sulphonic acid than was obtained by the separation of the sulphonchlorides.

3. Attempts to nitrate the sulphonchloride of p-xylene by means of various reagents met with only limited success. In all trials but one only one sulphonchloride, and that in small quantities, was produced, i. e., that of 3-nitro-1,4-dimethylbenzene-2-sulphonic acid. In one case a very small yield of the sulphonchloride of 6-nitro-1,4-dimethylbenzene-2-sulphonic acid was isolated. A rather large excess of nitrosulphuric acid gave the largest yield of nitrosulphonchloride.

4. Nitro-p-xylene is not easily sulphonated. Attempts to sulphonate this compound with sulphuric acid either at room temperature or on the water bath were not successful.

5. Chlorsulphonic acid acts upon nitro-p-xylene at the temperature of boiling water to produce in about equal amounts two nitrosulphonchlorides, i. e., 6-nitro-1,4-dimethylbenzene-2-sulphonchloride and 5-nitro-1,4-dimethylbenzene-2-sulphonchloride. A considerable amount of tarry matter is also formed. Of these two sulphonchlorides the last named is the less soluble and may be separated from the other by fractional crystallization from ether and petroleum ether.

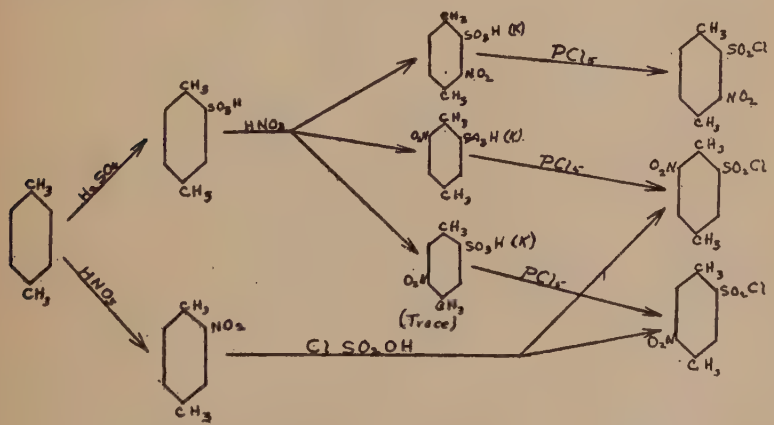
6. The configuration of the acids under consideration was determined by reducing them to the corresponding aminosulphonic acids and comparing the properties of these with the properties of the aminosulphonic acids described by Nolting and Kohn (Ber. 19, 141). Attempts to reduce 3-nitro-1,4-dimethylbenzene-2-sulphonic acid to the amino acid with hydrogen sulphide in alcoholic solu-

tion were not successful. When stannous chloride and hydrochloric acid were used reduction took place but the amino acid was at once hydrolized.

7. Besides the free acids the following derivatives of each of the three nitrosulphonic acids of p-xylene were prepared, described, and analysed: the sulphonchloride, the amide, the anilide, the phenyl ester, and the sodium, potassium, calcium, barium, and silver salts.

8. The 5-amino-1,4-dimethylbenzene-2-sulphonic acid was isolated and its properties studied as was also the barium salt of the 6-amino-1,4-dimethylbenezene-2-sulphonic acid.

9. The production of the sulphonchlorides of the three nitrosulphonic acids of p-xylene may be briefly represented by the following scheme:



10. This peculiar behavior may be accounted for in part by combining a number of the recently proposed theories of substitution. Stark (Ahren's Vortage XIX, 1, 25), Kauffmann (Ber. 45, 766-781), and Boeseken (Proc. K. Acad. Wetensch., Amsterdam (1912) 14, 1066) have proposed by various formulae the following hypothesis: The

fourth or residual valences of the carbon atoms of the benzene nucleus are delicately balanced and are therefore sensitive to the influence of substituents. It follows from this that the introduction of any substituent into the nucleus will disturb the balance or equilibrium in such a way as to modify the entire structure of the molecule, the degree of modification depending upon the specific nature of the substituent. If the position which a second or third substituent will take depends upon the condition of the fourth or residual valences, it follows that it will also depend upon the character and position of the substituents already present. In other words the position of the entering group will be largely determined by the groups already present in the molecule. Holleman (Ber. 44, 3556) has put forth the opinion that the position taken by the entering group is, with very few exceptions, determined by the groups already present and not by the character of the entering group. He, with others, has also pointed out (Ber. 44, 704; 2504, Rec. Trav. Chim. 30, 305) that catalytic agents and temperature influence the position of the entering group. Boeseken (loc. cit.) is of the opinion that a catalyst can cause a modification of both the benzene and the reacting molecule and that nitrogen pentoxide and sulphur trioxide act as catalysts in nitration and sulphonation.

Let us see how well the theories and the facts agree. If we obtain by nitrating nitro-p-xylene a mixture of the 6-2 and 3-2 dinitro compounds, and by nitrating p-xylene-sulphonic acid a mixture of the 6-nitro-2-sulphonic acid and 3-nitro-2-sulphonic acid (with a little of the 5-nitro-2-sulphonic acid) and if the position taken by the entering group is determined entirely by the groups already present it would seem that a nitro and a sulpho group have prac-

tically the same effect upon the fourth ("Gelockert") valences. We might then expect to obtain by the sulphonation of nitro-p-xylene with chlorsulphonic acid a mixture of the same two nitrosulphonic acids as were obtained by the nitration of p-xylenesulphonic acid. But we obtain a mixture of the 6-nitro-2-sulphonic acid and the 5-nitro-2-sulphonic acid.

We can stretch the theory to fit this fact by saying that the high temperature at which the sulphonation was carried out disturbed the equilibrium of the nucleus, or that the catalyst of the chlorsulphonic acid (whatever we may *assume* it to be) exerted a modifying influence upon the reaction. Although temperature and catalysts may modify the reaction to some extent it seems to the author that we have in this instance evidence of a certain amount of selective power on the part of the entering group. It may be that this selective power is brought into play by means of increased temperature or catalysts, or both, but it is still a selective power. It may be the greater size of the sulphonic acid group prevents it from taking the position ortho to the nitro group.

Flurscheim (Trans. Chem. Soc. 95, 718; 97, 84) has suggested a formula which explains the formation of ortho and meta derivatives, to the exclusion of the para derivative, by assuming that the ortho and meta positions are connected by a double bond. His formula fails to explain the formation of derivatives in which the substituent takes the ortho and meta positions to a group on opposite sides of the nucleus as is the case when nitro-p-xylene or p-xylenesulphonic acid or 1,2-dimethylbenzene-4-sulphonic acid is nitrated.

BIOGRAPHICAL SKETCH.

Ralph Chase Huston, the author of this dissertation, was born in Fairfield, Iowa, on the tenth day of March of the year 1885. He received his early education in the public schools of his native town, graduating from the High School in the year 1902. The following fall he entered Parsons College, at Fairfield, Iowa, where he majored in Biological and Physical Sciences and Mathematics, receiving the degree of Bachelor of Science in 1906.

The year following graduation he served as Instructor in Science in the High School at Junction City, Kansas. In the fall of 1907 he entered the State University of Iowa as a Scholar taking as his major Organic Chemistry and as his minor Physical Chemistry. In the spring of 1908 he was elected a member of the Society of the Sigma Xi and in July of the same year he received the degree of Master of Science. The following year he studied as a Fellow in the same University and was made Instructor in Chemistry for the Summer Session. In 1909 he was appointed Instructor in Chemistry in the State College of Washington where he remained until 1911 when he was appointed to an Assistant Professorship in the Michigan Agricultural College. Additional graduate work was done, in residence, during the summers of 1912 and 1913 and, in absentia, during the years 1911 to 1914 inclusive.

As a result of research carried out under the direction of Dr. Karslake the following articles have been published:

"The Action of Nitric Acid upon Benzoyl Chloride in the Presence of Acetic Anhydride." (Journ. Am. Chem. Soc. 31, 479.)

"6-Nitro-3-Methyl-4-Sulphobenzoic Acid and Some of Its Derivatives." (Journ. Am. Chem. Soc. 31, 1057.)